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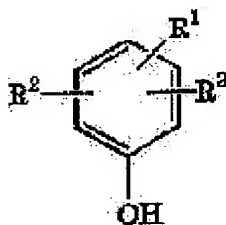
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(54) POSITIVE PHOTORESIST COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive photoresist composition superior in the balance of resist characteristics adapted to exposure to i rays.

SOLUTION: This positive phototresist composition comprises (A) an alkali- soluble phenol resin and (B) a 1,2-naphthoquinone-diazido-6-sulfonate photosensitive agent obtained by polycondensation of phenols and aldehydes or ketones represented by the formula and having a weight average molecular weight of 3000-12000 in terms of polystyrene measured by the pattern of the gel- permeation



chromatography using an ultraviolet 254nm detector and tetrahydrofuran. In the

formula, each of R1-R3 is an H atom or a 1-4C alkyl or alkoxy or hydroxy group.

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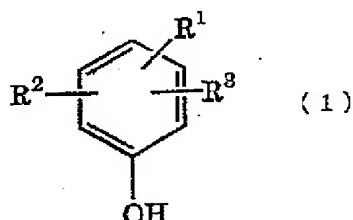
CLAIMS

[Claim(s)]

[Claim 1] (A) The positive-resist constituent characterized by being a positive-resist
constituent containing a 1 of polycondensation object with phenols, aldehydes, or
ketones expressed with alkali fusibility phenol resin and (B) following general formula
(1), and 2-naphthoquinonediazide-6-sulfonate system sensitization agent, and the
polystyrene equivalent weight mean molecular weights of the polycondensation object

concerned in the pattern obtained by the gel par MIESHON chromatography using the detector of UV254nm which used the tetrahydrofuran as the solvent being 3,000-12,000.

[Formula 1]



(R1-R3 show a hydrogen atom, a hydrogen atom, the alkyl group of carbon numbers 1-4, an alkoxy group, and hydroxyl among a formula (1).)

[Claim 2] Furthermore, the positive type photoresist constituent according to claim 1 which uses together a 1 and 2-naphthoquinonediazide-5-sulfonate or 1, and 2-naphthoquinonediazide-4-sulfonate as a sensitization agent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive-resist constituent for micro processing required for manufacture of a semiconductor device, a magnetic-bubble-memory component, an integrated circuit, etc. in more detail about a positive-resist constituent.

[0002]

[Description of the Prior Art] As a resist constituent for forming a semiconductor device, a positive-resist constituent is more in use than a negative-resist constituent in recent years. Although a negative-resist constituent is high sensitivity, this originates in swelling being large and a difficulty being in definition, in order to use an organic solvent for development. On the other hand, it is thought that it can respond to high integration of a semi-conductor enough since a positive-resist constituent can be developed with an alkali water solution with little swelling and is moreover excellent in definition. Conventionally, the positive-resist constituent generally used in this field consists of alkali fusibility resin, such as novolak resin, and a quinone JIAJI

sulfonic-acid compound. This positive-resist constituent does not have swelling in order to perform development by the alkali water solution, and it is excellent in definition. Moreover, resolution of a positive-resist constituent [such] improves further by high performance-ization of engine-performance amelioration of itself, and an exposure machine, and the formation of a detailed pattern 0.5 micrometers or less of it has also been attained.

[0003] However, it is not obtained but much more improvement in the engine performance is desired by the result with the conventional positive-resist constituent not necessarily satisfactory in respect of many properties, such as sensibility, a remaining rate of membrane, resolution, thermal resistance, and preservation stability. It is necessary to control a resist dimension more severely in detailed pattern formation 0.5 micrometers or less especially, therefore a positive-resist constituent with more sufficient dimensional accuracy is called for strongly. From such a viewpoint, the 1 of various phenolic compounds and 2-quinone diazide-4-sulfonate or 1, and 2-quinone diazide-5-sulfonate has been conventionally used as a sensitization agent. For example, phenols, and aldehydes or ketones is made to react to JP,4-230755,A, a phenolic compound of a certain kind with low weight average molecular weight is obtained, and the approach of forming this into a quinone diazide-5-sulfonate and making it into a sensitization agent is indicated. However, according to our knowledge, even if it used the sensitization agent currently indicated by this official report, sensibility sufficient in exposure by i line was not obtained. Thus, although the sensitization agent examined conventionally has some which give a good resist property by g line (436nm) exposure In i line (365nm) exposure, with the thick film beyond this of what can demonstrate the engine performance, since these sensitization agents had the large exposure absorption of light of a sensitization agent, they had the problem that a practical pattern was not obtained at the thickness of 1-micrometer or less extent.

[0004] As a means to obtain a practical pattern by i line exposure, using ester with an 1,2-naphthoquinone-2-diazido-6-sulfonic acid, alcohols, or phenols, the sulfonamide of an 1,2-naphthoquinone-2-diazido-6-sulfonic acid and organic amines, etc. as a dissolution retardant (it functioning as a sensitization agent) is proposed (JP,4-153656,A). Although many open patent official reports are mentioned to the official report concerned as phenols, great research is needed when the property of a sensitization agent chooses the phenols from which the effectiveness which may change with classes of phenols and was excellent is acquired.

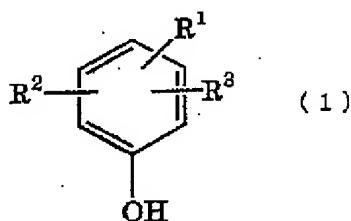
[0005]

[Problem(s) to be Solved by the Invention] Under this conventional technique, as a result of inquiring wholeheartedly in order to obtain the resist constituent in which the good resist property of balance is shown by i line exposure, by using a 1 and 2-naphthoquinonediazide-6-sulfonate using the polycondensation object of phenols, aldehydes, or ketones, artificers find out that the outstanding pattern configuration is shown and came to complete this invention.

[0006]

[Means for Solving the Problem] According to this invention, in this way (A) alkali fusibility phenol resin, (B) It is a positive-resist constituent containing a 1 of polycondensation object with phenols, aldehydes, or ketones expressed with following general formula (1), and 2-naphthoquinonediazide-6-sulfonate system sensitization agent. With the gel par MIESHON chromatography using the detector of UV254nm which used the tetrahydrofuran as the solvent The positive-resist constituent characterized by the polystyrene equivalent weight mean molecular weights of the polycondensation object concerned in the obtained pattern being 3,000-12,000 is offered.

[Formula 2]



(R1-R3 show a hydrogen atom, a hydrogen atom, the alkyl group of carbon numbers 1-4, an alkoxy group, and hydroxyl among a formula (1).)

[0007] Hereafter, this invention is explained in full detail.

(A) In alkali fusibility phenol resin this invention, two or more kinds can be mixed and alkali fusibility phenol resin can also be used, even if independent. As an example of alkali fusibility phenol resin, the condensation reaction product of phenols and aldehydes, the condensation reaction product of phenols and ketones, a vinyl phenol system polymer, an isopropenyl phenol system polymer, the hydrogenation resultant of these phenol resin, etc. can be mixed and used, for example. As an example of the phenols used here A phenol, o-cresol, m-cresol, p-cresol, 2, 3-dimethylphenol, 2, 5-dimethylphenol, 3, 4-dimethylphenol, 3, 5-dimethylphenol, 2, 4-dimethylphenol, 2, 6-dimethylphenol, 2 and 3, a 5-trimethyl phenol, 2, 3, a 6-trimethyl phenol,

2-*t*-butylphenol, 3-*t*-butylphenol, 4-*t*-butylphenol, 2-methyl resorcinol, 4-methyl resorcinol, 5-methyl resorcinol, 4-*t*-butyl catechol, 2-methoxy phenol, 3-methoxy phenol, 2-propyl phenol, 3-propyl phenol, 4-propyl phenol, 2-isopropyl phenol, 3-isopropyl phenol, 4-isopropyl phenol, 2-methoxy-5-methyl phenol, 2-*t*-butyl-5-methyl phenol, Timor, an iso thymol, pyrogallol, etc. are illustrated. *o*-cresol, *m*-cresol, *p*-cresol, 2, 3-dimethylphenol, 3, 4-dimethylphenol, 3, 5-dimethylphenol, 2, 5-dimethylphenol, 2 and 3, a 5-trimethyl phenol, 2 and 3, a 6-trimethyl phenol, etc. are desirable examples among these. These compounds can also be used combining independent or two kinds or more.

[0008] As an example of aldehydes, formalin, a paraformaldehyde, A trioxane, an acetaldehyde, a propyl aldehyde, a benzaldehyde, Phenylacetaldehyde, alpha-phenylpropyl aldehyde, beta-phenylpropyl aldehyde, Ortho hydroxybenzaldehyde, an *m*-hydroxy benzaldehyde, A *p*-hydroxy benzaldehyde, *o*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *o*-nitro benzaldehyde, *m*-nitro benzaldehyde, *p*-nitro benzaldehyde, *o*-methyl benzaldehyde, *m*-methyl benzaldehyde, *p*-methyl benzaldehyde, *p*-ethyl benzaldehyde, a *p*-*n*-butyl benzaldehyde, a terephthal aldehyde, etc. are illustrated. Formalin, a paraformaldehyde, and hydroxy benzaldehydes are [among these] desirable. These compounds can also be used combining independent or two kinds or more. As an example of ketones, an acetone, a methyl ethyl ketone, a diethyl ketone, diphenyl ketone, etc. are illustrated. These compounds can also be used combining independent or two kinds or more. These condensation reaction products can be obtained by making a conventional method, for example, phenols, aldehydes, or ketones react under acid catalyst existence.

[0009] A vinyl phenol system polymer is chosen from the homopolymer of a vinyl phenol, and the copolymer of a vinyl phenol and a copolymerizable component, and isopropenyl phenol system polymers are the homopolymer of an isopropenyl phenol, and a copolymer of an isopropenyl phenol and a copolymerizable component. As an example of a vinyl phenol, an isopropenyl phenol, and a copolymerizable component, an acrylic acid, a methacrylic acid, styrene, a maleic anhydride, maleic-acid imide, vinyl acetate, acrylonitrile, these derivatives, etc. are illustrated. A copolymer is obtained by the well-known approach. The hydrogenation resultant of phenol resin dissolves a conventional method, for example, the above-mentioned phenol resin, in an organic solvent, and is acquired by performing hydrogenation under existence of a homogeneous system or a heterogeneous catalyst.

[0010] the time of measuring the polystyrene equivalent weight average molecular

weight (only henceforth average molecular weight or Mw) in the pattern obtained by the gel par MIESHON chromatography using the detector of UV254nm which used as the solvent the tetrahydrofuran of the alkali fusibility phenol resin used in this invention, using a tetrahydrofuran as a solvent -- usually -- 2,000-25,000 -- it is 3,500-20,000 preferably. Average molecular weight is in the inclination for a pattern configuration, resolution, and development nature to get worse less than by 3,500, and is not practical at less than 2,000. Moreover, it is not practical if a pattern configuration, development nature, and sensibility will get worse if 20,000 is exceeded, and especially 25,000 is exceeded.

[0011] These alkali fusibility phenol resin can also be used as what controlled molecular weight and molecular weight distribution by the well-known means. As an approach of controlling molecular weight and molecular weight distribution, resin is crushed, solid liquid extraction is carried out by the organic solvent with suitable solubility, or resin is dissolved in a good solvent, and it is dropped into a poor solvent, or a poor solvent is dropped, and approaches, such as **-liquid or carrying out liquid-liquid extraction, are mentioned.

[0012] (B) Use a 1 of phenols [which are expressed with said general formula (1) as a sensitization agent], aldehydes, or ketones, and 2-naphthoquinonediazide-6-sulfonate compound (it may be hereafter called the sensitization agent of this invention) in sensitization agent this invention.

[0013] The phenols used here are compounds expressed with said formula (1). As an example of the substituents R1-R3 in a formula (1) A hydrogen atom, a hydroxyl group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, The alkyl group of the carbon numbers 1-4, such as n-butyl, an isobutyl radical, s-butyl, and t-butyl; A methoxy group, An ethoxy radical, n-propoxy group, an isopropoxy group, an n-butoxy radical, It is hydroxyl; The alkoxy group of the carbon numbers 1-4, such as an iso butoxy radical, an s-butoxy radical, and a t-butoxy radical; as substituents other than a hydrogen atom It is a methyl group or hydroxyl preferably, and it is desirable 1 or to combine two substituents other than a hydrogen atom and one hydroxyl group. The same thing as the phenols which became the alkali fusibility phenol resin raw material mentioned later as an example of such phenols is mentioned. A phenol, o-cresol, m-cresol, p-cresol, 3, 5-dimethylphenol, 2, 5-dimethylphenol, 2, 3-dimethylphenol, 3, 4-dimethylphenol, 2, 3, a 5-trimethyl phenol, 3 and 4, a 5-trimethyl phenol, resorcinol, 2-methyl resorcinol, pyrogallol, etc. are desirable, and are especially an example with desirable phenol, o-cresol, m-cresol, and p-cresol. Moreover, the aldehydes or ketones which carries out a polycondensation to this also serves as the

below-mentioned alkali fusibility phenol resin raw material, and it is especially an example with desirable formaldehyde, formalin, and acetaldehyde. What is necessary is just to make phenols, aldehydes, or ketones react under acid catalyst existence like [the synthetic approach of such a polycondensation object] the synthetic approach of the below-mentioned alkali fusibility phenol resin.

[0014] the weight average molecular weight (only henceforth weight average molecular weight) measured by the gel par MIESHON chromatography with which this polycondensation object used the tetrahydrofuran as the solvent -- 3,000-12,000 -- desirable -- 3,000-10,000 -- it is 4,000-9,000 more preferably. Weight average molecular weight crushes resin, solid liquid extraction of it can be carried out by the organic solvent with suitable solubility, or it can dissolve resin in a good solvent, and can be dropped into a poor solvent, or can trickle a poor solvent, and can adjust it by **-liquid, carrying out liquid-liquid extraction, etc.

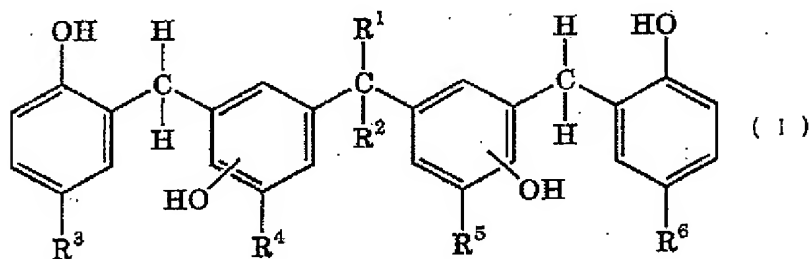
[0015] Thus, the ester of this invention can be obtained by making the obtained polycondensation object react under organic base existence, such as inorganic bases, such as a sodium carbonate, a sodium hydrogencarbonate, a sodium hydroxide, and a potassium hydroxide, or a trimethylamine, triethylamine, tripropylamine, diisopropylamine, tributylamine, a pyrrolidine, a piperidine, a piperazine, a morpholine, a pyridine, and dicyclohexylamine, in solvents, such as 1 and 2-naphthoquinonediazide-6-sulfonic-acid halide, an acetone and dioxane, and a tetrahydrofuran. the inside of all the phenolic hydroxyl groups of the above-mentioned condensate, and 1 and the rate (henceforth the rate of esterification) formed into a 2-naphthoquinonediazide-6-sulfonate -- usually -- it is 40 - 60% of thing more preferably 30 to 65% 10 to 70%. It is in the inclination for preservation stability to fall and for a good pattern configuration not to be acquired and is not desirable if this rate of esterification is too high.

[0016] Of course, 1 of the well-known phenolic compound of others besides the sensitization agent of this invention mentioned above, a 2-naphthoquinonediazide-6-sulfonate compound, A 1 and 2-naphthoquinonediazide-5-sulfonate or 1, and 2-naphthoquinonediazide-4-sulfonate can be used together as a sensitization agent. Since the improvement in the dissolution suppression effectiveness over an alkali developer etc. is expectable especially, concomitant use of a 1 and 2-naphthoquinonediazide-5-sulfonate or a 1 and 2-naphthoquinonediazide-4-sulfonate is an especially desirable mode.

[0017] As the raw material of the sensitization agent used together here, i.e., an

example of a mother-nucleus compound of having a phenolic hydroxyl group 2, 3, 4-trihydroxy benzophenone, 2 and 4, a 4'-trihydroxy benzophenone, A 2, 3, 4, and 4'-tetra-hydroxy benzophenone, 2 and 4, 2', 4'-tetra-hydroxy benzophenone, Polyhydroxy benzophenones, such as 2, 3, 4, 2', and a 4'-pentahydroxy benzophenone; Gallic-acid methyl, Gallate, such as gallic-acid ethyl and propyl gallate; A 2 and 2-bis(4-hydroxyphenyl) propane, Polyhydroxy screw phenyl alkanes, such as a 2 and 2-bis(2, 4-dihydroxy phenyl) propane; Tris (4-hydroxyphenyl) methane, 1, 1, and 1-tris (4-hydroxy-3-methylphenyl) ethane, 1, 1, and 1-tris (4-hydroxy-3-methylphenyl) ethane, 1, 1, and 1-tris (4-hydroxyphenyl) ethane, 1, and 1-bis(4-hydroxy-3-methylphenyl)-1-(4-hydroxyphenyl) ethane, Polyhydroxy tris phenyl alkanes, such as a bis(4-hydroxy-3-methylphenyl)-2-hydroxy-4-methoxy phenylmethane; 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane, 1, 1, 2, and 2-tetrakis (3-methyl-4-hydroxyphenyl) ethane, Polyhydroxy tetrakis phenyl alkanes, such as 1, 1, 3, and 3-tetrakis (4-hydroxyphenyl) propane; alpha, alpha, alpha', an alpha'-tetrakis (4-hydroxyphenyl)-3-xylene, alpha, alpha, alpha', an alpha'-tetrakis (4-hydroxyphenyl)-4-xylene, Polyhydroxy tetrakis phenyl xylenes, such as alpha, alpha, alpha', and an alpha'-tetrakis (3-methyl-4-hydroxyphenyl)-3-xylene; 2, 6-bis(2, 4-dihydroxy benzyl)-p-cresol, 2, 6-bis(2, 4-dihydroxy-3-methylbenzyl)-p-cresol, 4, 6-bis(4-hydroxybenzyl) resorcinol, 4, 6-bis(4-hydroxy-3-methylbenzyl) resorcinol, 4, 6-bis(4-hydroxybenzyl)-2-methyl resorcinol, The compound (tetramer of a phenol system compound and formalin) shown by the trimer of phenols, such as 4 and 6-bis(4-hydroxy-3-methylbenzyl)-2-methyl resorcinol, and formalin and the following general formula (I) is mentioned.

[Formula 3]



(R1 and R2 are a hydrogen atom or the alkyl group of carbon numbers 1-4 mutually-independent among a formula, and R3-R6 are the alkyl groups of carbon numbers 1-4 mutually-independent.)

[0018] In a sensitization agent, others [radical / of the 1 and 2-naphthoquinonediazide-6-sulfonic-acid origin / sensitization], Although the rate of

concomitant use can be set as arbitration in consideration of the mother nucleus which has the phenolated water acid radical of the rate of esterification, or a sensitization agent when the sensitization radical of the 1, 2-naphthoquinonediazide-5-sulfonic-acid and 1, and 2-naphthoquinonediazide-4-sulfonic-acid origin is used together. Usually, it is desirable 1:99-99:1, and to set up in 5:95-95:5 preferably by the ratio (mole ratio) of the sensitization radical of the 1 and 2-naphthoquinonediazide-6-sulfonic-acid origin and the other sensitization radical. moreover, the case where the sensitization agent which are sensitization agents other than this invention, and has the sensitization radical of the 1 and 2-naphthoquinonediazide-6-sulfonic-acid origin is used -- all -- the sensitization radical of the sensitization agent origin of the inside of the sensitization radical of the 1 and 2-naphthoquinonediazide-6-sulfonic-acid origin, and this invention -- comparatively (mole ratio) -- usually -- it is 85% or more more preferably 70% or more 50% or more. The rate of esterification of the sensitization agent at the time of using as a mother-nucleus compound the polycondensation object which the ratio (rate of average esterification) of esterification of the naphthoquinonediazide sulfonic-acid compound to the phenolic hydroxyl group of the sensitization agent used by this invention is chosen as arbitration by the class of mother-nucleus compound, and has been mentioned above is as having indicated in the term of the ester of said this invention. About the ester of this invention, if the ratio of esterification is too low, degradation of a pattern configuration or definition will be imitated and it will come, and when the ratio of esterification is too high, there is loam Lycium chinense about the fall of sensibility.

[0019] (C) In phenolic compound this invention, as an arbitration component, in order to improve resist properties, such as a pattern configuration, thermal resistance, and sensibility, a phenolic compound can be added. That for which such a phenolic compound is usually used as an additive of a resist constituent is mentioned. As an example Mono-phenols, such as p-phenylphenol and p-isopropyl phenol; Biphenol, A - dihydroxy diphenyl ether, and 4 and 4'4, 4'-dihydroxy benzophenone, Bisphenol A (Honshu Chemical Industry Co., Ltd. make), Bisphenol C (Honshu Chemical Industry Co., Ltd. make) Bisphenol E (Honshu Chemical Industry Co., Ltd. make), Bisphenol F (Honshu Chemical Industry Co., Ltd. make) Bisphenol A P (Honshu Chemical Industry Co., Ltd. make), Bisphenol M (Mitsui Petrochemical Industries, Ltd. make) Bisphenol P (Mitsui Petrochemical Industries, Ltd. make), Bisphenol Z (Honshu Chemical Industry Co., Ltd. make) A 1 and 1-bis(4-hydroxyphenyl) cyclopentane, 9, and 9-bis(4-hydroxyphenyl) fluorene, Bisphenols, such as a 1 and

1-bis(5-methyl-2-hydroxyphenyl) methane, 3, and 5-dimethyl-4-hydroxybenzyl phenol; 1, 1, and 1-tris (4-hydroxyphenyl) methane, 1, 1, and 1-tris (4-hydroxyphenyl) ethane, 1, and 1-bis(3-methyl-4-hydroxyphenyl)-1-(4-hydroxyphenyl) methane, 1 and 1-bis(2, 5-dimethyl-4-hydroxyphenyl)-1-(2-hydroxyphenyl) methane, 1 and 1-bis(3, 5-dimethyl-4-hydroxyphenyl)-1-(2-hydroxyphenyl) methane, 2, 6-bis(5-methyl-2-hydroxybenzyl)-4-methyl phenol, 2, 6-bis(4-hydroxybenzyl)-4-methyl phenol, 2, 6-bis(3-methyl-4-hydroxybenzyl)-4-methyl phenol, 2, 6-bis(3, 5-dimethyl-4-hydroxybenzyl)-4-methyl phenol, Tris phenols, such as tris phenol-PA (Honshu Chemical Industry Co., Ltd. make) and tris phenol-TC (Honshu Chemical Industry Co., Ltd. make); 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane, 1, 1, 2, and 2-tetrakis (3-methyl-4-hydroxyphenyl) ethane, 1, 1, 3, and 3-(4-hydroxyphenyl) propane, 1, 1 and 5, 5-tetrakis (4-hydroxyphenyl) pentane, alpha, alpha, alpha', an alpha'-tetrakis (4-hydroxyphenyl)-3-xylene, alpha, alpha, alpha', an alpha'-tetrakis (4-hydroxyphenyl)-4-xylene, Tetrakis phenols, such as an alpha, alpha, alpha', and alpha'-tetrakis (3-methyl-4-hydroxyphenyl)-3-xylene, alpha and alpha, alpha', alpha'-tetrakis (3-methyl-4-hydroxyphenyl)-4-xylene, etc. are illustrated.

[0020] (C) The phenolic compound as a component can use one kind of arbitration, or two kinds or more, and when resin with few ratios which contain the thing of the molecular weight of ten or less nuclides of alkali fusibility resin (A) especially is chosen, if such a phenolic compound is used together, a good result will be obtained in many cases. Although the addition can be chosen as arbitration, it is usually below 30 weight sections more than 3 weight sections preferably below 40 weight sections more than 1 weight section to the alkali fusibility phenol resin 100 weight section.

[0021] The positive-resist constituent of this invention is usually dissolved and used for a solvent, in order to apply to a substrate and to form the resist film. As an example of an usable solvent, in this invention Ketones, such as an acetone, a methyl ethyl ketone, cyclopentanone, and a cyclohexanone; N-propyl alcohol, Alcohols, such as isopropyl alcohol, n-butyl alcohol, and a cyclohexanol; Ethylene glycol wood ether, Ether, such as ethylene glycol diethylether and dioxane; Ethylene glycol monomethyl ether, Alcoholic ether, such as ethylene glycol monoethyl ether; Formic-acid propyl, Formic-acid butyl, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, Ester, such as methyl butyrate, ethyl butylate, methyl lactate, and ethyl lactate; A cellosolve acetate, Methyl-cellosolve acetate, ethylcellosolve acetate, a propyl cellosolve acetate, Cellosolve acetates, such as butyl-cellosolve acetate; Propylene glycol, Propylene-glycol-monomethyl-ether acetate, propylene glycol monoethyl

ether acetate, Propylene glycols, such as the propylene glycol monobutyl ether; The diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, diethylene-glycols [, such as diethylene-glycol diethylether,]; -- halogenated hydrocarbon [, such as a trichloroethylene,]; -- toluene -- Aromatic hydrocarbon, such as a xylene; polar solvents, such as dimethylacetamide, dimethylformamide, and N-methyl acetamide, etc. are mentioned, these may be independent, or two or more sorts may be mixed and used for them.

[0022] In order to improve development nature, preservation stability, thermal resistance, etc. if needed to the positive-resist constituent of this invention, a copolymer with styrene, an acrylic acid, a methacrylic acid, or a maleic anhydride, the copolymer of an alkene and a maleic anhydride, a vinyl alcohol polymer, a vinyl-pyrrolidone polymer, rosin, a shellac, etc. can be added. the addition of such a polymer -- the total alkali fusibility phenol resin 100 weight section -- receiving -- the above-mentioned polymer 0 - 50 weight sections -- it is 5 - 20 weight section preferably.

[0023] The positive-resist constituent of this invention can be made to contain the additive which has the compatibility of a surfactant, a preservation stabilizer, a sensitizer, a striae SHON inhibitor, a plasticizer, etc. if needed.

[0024] As a surface active agent, for example The polyoxyethylene lauryl ether, Polyoxyethylene alkyl ETERU, such as polyoxyethylene stearylether and the polyoxyethylene oleyl ether; Polyoxyethylene octyl phenyl ether, Polyoxyethylene aryl ether, such as the polyoxyethylene nonyl phenol ether; A polyethylene-glycol JIRAU rate, Polyethylene-glycol dialkyl ester, such as ethylene glycol distearate; EFUTOPPU EF301, EF303, and EF352 (new Akita formation shrine make), The megger facsimile F171, F172, F173, and F177 (Dainippon Ink make), Fluorad FC430 and FC431 (Sumitomo 3M make), Asahi guard AG710 and Sir chlorofluocarbon Fluorine surfactant; organosiloxane polymer, such as S-382, SC-101, SC-102, SC-103, SC-104, SC-105, and SC-106 (Asahi Glass Co., Ltd. make) KP341 (Shin-Etsu Chemical Co., Ltd. make); [Acrylic-acid system] Or methacrylic-acid system (**) polymer poly flow No.75 and No.95 (the Kyoisha fats-and-oils chemical-industry company make) are mentioned. The loadings of these surfactants are usually below 1 weight section preferably below 2 weight sections per solid content 100 weight section of a constituent.

[0025] Thus, the resist property in which A parameter with which the obtained resist constituent is computed by the following type (1) usually maintained the balance by i line exposure is acquired, and what is 1.20 or less [0.4 or more] 1.35 or less [0.35 or

more] preferably 1.50 or less [0.30 or more] is especially more preferably desirable. In addition, T_r of resist thickness and T_{max} is [the permeability after exposure and T_0] the permeability before exposure among said formula. Transmission T_{max} and T_0 are the transmission (T_{max}) when applying a resist constituent so that it may be set to 1 micrometer on a glass substrate, and the transmission (T_0) when carrying out full bleach using PLA-501F (canon company make) after spreading, and are measured here using UV spectrophotometric measurement machine, respectively.

[0026]

[Formula 1]

$$A = \frac{1}{T_r} \ln (T_{max} / T_0) \quad (1)$$

[0027] Although A parameter is a parameter with the largest effect by the sensitization agent component, since the constituent included in the range of above-mentioned [this parameter] gives the resist property which maintained the balance by i line exposure, it is especially desirable.

[0028] Although the resist constituent of this invention usually uses an alkali water solution as an alkali developer As an example, a sodium hydroxide, a potassium hydroxide, a sodium silicate, The water solution of inorganic alkali, such as ammonia; The water-solution; diethylamine of primary amines, such as ethylamine and propylamine, The water solution of secondary amines, such as a dipropyl amine; The water-solution; diethyl ethanolamine of tertiary amines, such as a trimethylamine and triethylamine, The water solution of alcoholic amines, such as triethanolamine; Tetramethylammonium hydroxide, Tetraethylammonium hydroxide, trimethyl hydroxymethyl ammonium hydroxide, The water solution of quaternary ammonium hydroxide, such as triethyl hydroxymethyl ammonium hydroxide and trimethylhydroxyethylammonium hydroxide, etc. is mentioned. Moreover, water-soluble organic solvents, such as a methanol, ethanol, propanol, and ethylene glycol, a surfactant, the dissolution retardant of resin, etc. can be added in the above-mentioned alkali water solution if needed.

[0029] After applying the resist solution made to dissolve the resist constituent of this invention in a solvent to substrate front faces, such as a silicon wafer, with a conventional method, the resist film can be formed by carrying out desiccation removal of the solvent. Spin coating is encouraged especially as the method of application at this time. Thus, as a source of exposure used for the obtained resist film by the exposure for making a pattern form, sources of an electron ray, such as

ultraviolet rays, far ultraviolet rays, KrF excimer laser light, an X-ray, and an electron ray, are mentioned. Furthermore, when it heat-treats after exposure (after [exposure] BEKU), since sensibility, a remaining rate of membrane and resolution, and heat-resistant improvement can be aimed at, it is desirable.

[0030]

[Example] A synthetic example and an example are given to below and this invention is explained to it still more concretely. In addition, the section in each example and % are weight criteria as long as there is no notice especially. Moreover, the measured weight average molecular weight (it is called Mw) is the polystyrene equivalent weight average molecular weight (Mw) in the pattern obtained by the gel par MIESHON chromatography using the detector of UV254nm which used the tetrahydrofuran as the solvent.

[0031] (Synthetic example 1) It was made to react for 2 hours, putting m-cresol 360g, 360g [of p-cresol], and 37% formalin 372g, and 2.45g of oxalic acid 2 hydrates into the 2l. flask equipped with the synthetic cooling pipe and stirring equipment of novolak resin A-1, and keeping at 95-100 degrees C. Then, after decompressing to 10mmHg(s) and removing an unreacted monomer and water, having distilled off water over 2 hours and carrying out a temperature up to 180 degrees C further at 100-105 degrees C, it returned and collected to the room temperature and 592g of novolak resin A-1 was obtained. Mw of this novolak resin A-1 was 5500.

[0032] (Synthetic example 2) 385g and ethylcellosolve acetate 350g were added, and the novolak resin A-1 obtained in the example 1 of the synthetic above-mentioned composition of novolak resin A-2 was dissolved. The flask was equipped with the tap funnel, where temperature is controlled at 80-85 degrees C, toluene 3450g was dropped from the tap funnel, and it heated at 80 more degrees C for 1 hour. To the room temperature, it cooled slowly and put for further 1 hour. After the decantation removed the supernatant of a pitch which has deposited, 570g of ethyl lactates was added, it heated at 100 degrees C by 100mmHg, residual toluene was removed, and the ethyl lactate solution of novolak resin A-2 was obtained. Mw of this novolak resin A-2 was 8000.

[0033] (Synthetic example 3) It was made to react for 2 hours, putting m-cresol 280g, 421g [of p-cresol], and 37% formalin 343g, and 2.45g of oxalic acid 2 hydrates into the 2l. flask equipped with the synthetic cooling pipe and stirring equipment of novolak resin A-3, and keeping at 95-100 degrees C. Then, after having carried out, having distilled off water over 2 hours and carrying out a temperature up to 180 degrees C further at 100-105 degrees C, decompressing to 10mmHg(s) and removing an

unreacted monomer and water, it returned and collected to the room temperature and 473g was obtained for novolak resin A-3. Mw of this novolak resin A-3 was 6300.

[0034] (Synthetic example 4) Novolak resin A-3 obtained in the example 3 of the acquisition above-mentioned composition of novolak resin A-4 380g and ethylcellosolve acetate 350g were added, and it dissolved. The flask was equipped with the tap funnel, where temperature is controlled at 80-85 degrees C, toluene 3450g was dropped, and it heated at 80 more degrees C for 1 hour. To the room temperature, it cooled slowly and put for further 1 hour. After the decantation removed the supernatant of a pitch which has deposited, 570g of ethyl lactates was added, it heated at 100 degrees C by 100mmHg, residual toluene was removed, and the ethyl lactate solution of novolak resin A-4 was obtained. Mw of this novolak resin A-4 was 9700.

[0035] (Synthetic example 5) It was made to react for 2 hours, putting m-cresol 291g, 221g [of p-cresol], and 37% formalin 523g, and 2.45g of oxalic acid 2 hydrates into the 2l. flask equipped with the synthetic cooling pipe and stirring equipment of novolak resin A-5, and keeping at 95-100 degrees C. Then, after having carried out, having distilled off water over 2 hours and carrying out a temperature up to 180 degrees C further at 100-105 degrees C, decompressing to 10mmHg(s) and removing an unreacted monomer and water, it returned and collected to the room temperature and 489g of novolak resin A-5 was obtained. Mw of this novolak resin A-5 was 8500.

[0036] (Synthetic example 6) Novolak resin A-5 obtained in the example 5 of the acquisition above-mentioned composition of novolak resin A-6 350g and ethylcellosolve acetate 340g were added, and it dissolved. The flask was equipped with the tap funnel, and where temperature is controlled at 80-85 degrees C, after dropping toluene 3400g and heating at 80 more degrees C for 1 hour, it cooled slowly to the room temperature and put for further 1 hour. After the decantation removed the supernatant of a pitch which has deposited, 570g of ethyl lactates was added, it heated at 100 degrees C by 100mmHg, residual toluene was removed, and the ethyl lactate solution of novolak resin A-6 was obtained. Mw of this novolak resin A-6 was 11100.

[0037] (Synthetic example 7) It was made to react for 5 hours, putting m-cresol 203.5g, 271.4g [of p-cresol], and 37% formalin 223.2g, and 15.0g of oxalic acid 2 hydrates into the 2l. flask equipped with the synthetic cooling pipe and stirring equipment of novolak resin A-7, and keeping at 95-100 degrees C. Then, after decompressing to 10mmHg(s) and removing an unreacted monomer and water, having distilled off water over 2 hours and carrying out a temperature up to 195 more

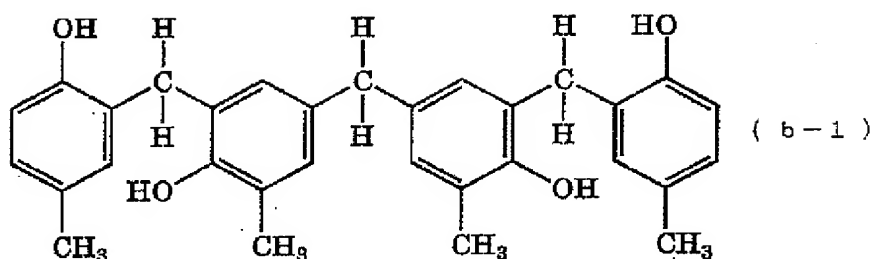
degrees C at 100–105 degrees C, it returned and collected to the room temperature and novolak resin A-7 was obtained. Mw of this novolak resin A-7 was 2300.

[0038] (Synthetic example 8) It was made to react for 3 hours, putting m-cresol 353.5g, 151.4g [of p-cresol], and 37% formalin 533.2g, and 3.0g of oxalic acid 2 hydrates into the 2l. flask equipped with the synthetic cooling pipe and stirring equipment of novolak resin A-8, and keeping at 95–100 degrees C. Then, after decompressing to 10mmHg(s) and removing an unreacted monomer and water, having distilled off water over 2 hours and carrying out a temperature up to 195 degrees C further at 100–105 degrees C, it returned and collected to the room temperature and novolak resin A-8 was obtained. Mw of this novolak resin A-8 was 13100.

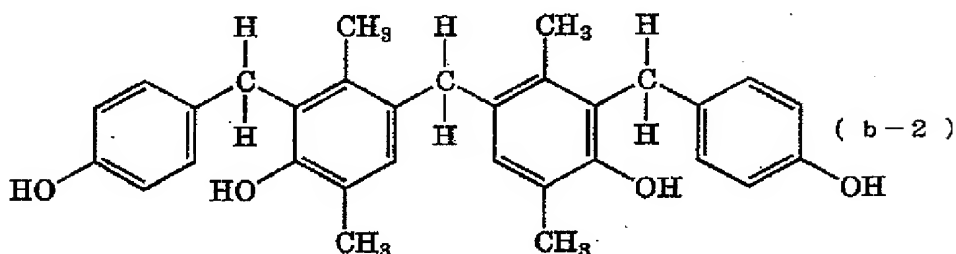
[0039] (Synthetic examples 9–16) As synthetic phenol of the sensitization agent B-1 to B-8, using the various novolak resin obtained in the synthetic examples 1–8, 1 and 2-naphthoquinonediazide-6-sulfonic-acid chloride (mol by which an amount is equivalent to the rate of esterification in Table 1 number) was dissolved in the acetone, and it considered as the solution of concentration 10%. It was dropped having applied it for 30 minutes for the 1.2 equivalence of 1 and 2-naphthoquinonediazide-6-sulfonic-acid chloride controlling temperature at 20–25 degrees C, it held at this temperature for further 2 hours, and the reaction was completed. The salt which has deposited was carried out the ** exception and it supplied to 0.2% oxalic acid water solution of the amount of 10 times of reaction mixture. The solid content which has deposited was filtered, with ion exchange water, after washing, the vacuum drying was carried out and the naphthoquinonediazide sulfonate system sensitization agent B-1 to B-8 was obtained.

[0040] As synthetic phenol of the sensitization agent B-9 to B-11, a bottom type (b-1), (Synthetic examples 17–19) Or (b-3) use and 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride (mol by which an amount is equivalent to the rate of esterification in Table 1 number) is made to react by the same approach as the synthetic example 9. (b-2) The naphthoquinonediazide sulfonate system sensitization agent B-9 corresponding to each phenols, B-10, and B-11 were obtained.

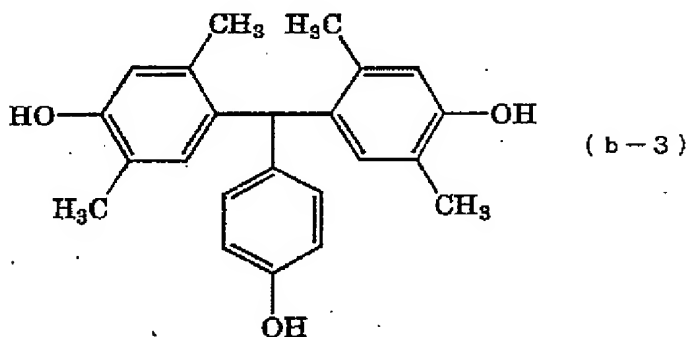
[Formula 4]



[Formula 5]



[Formula 6]



[0041] (Examples 1-9, examples 1 and 2 of a comparison) The novolak resin and the sensitization agent which were obtained in the synthetic example, phenols, and a surfactant were dissolved in the solvent, the positive type photoresist constituent of the presentation which filters with a 1.17-micrometer Teflon filter (polytetrafluoroethylene filter), and is shown in Table 1 was prepared, and the resist engine performance of the constituent concerned was evaluated. In addition, all evaluations are performed on a silicon wafer.

[0042] (1) The value which expressed with the exposure time (unit: msec) the amount of exposure energy which a 1:1 line & tooth space with a sensibility of 0.60 micrometers can form as a design dimension.

(2) Express the minimum pattern dimension (micrometer) resolved when it exposes by

the resolution above-mentioned exposure time.

(3) The wafer in which the pattern configuration resist pattern was formed was cut from the perpendicular direction of the Rhine pattern, and the result observed with the electron microscope from the direction of a cross section of a pattern was shown. the thing which has ** and film decrease in some which have started that to which does not have film decrease and the pattern sidewall has started at the include angle of 80 degrees or more to the substrate at the include angle of O and 70 degrees [less than 80] or more, and a sidewall -- a substrate -- receiving -- the thing of less than 70 degrees -- x -- ** -- it carried out.

(4) The deflection width of face of a focus in case the 1:1 line & tooth space of 0.35 micrometers of focal admissibility is less than **10% of the design dimension of a mask and a remaining rate of membrane (ratio of the resist thickness before and behind the development of the part in which a pattern is not formed on the wafer (%)) is 90% or more estimated focal admissibility. The deflection width of face of a focus made x O and a less than 1.2-micrometer thing for what is 1.2 micrometers or more.

(5) In the resist thickness of 1.07 micrometers of dimensional changes, with the light exposure reproducing the mask dimension of 0.35 micrometers, the mask dimension was observed how and what is ** and 16% or more about what is O and 11 - 15% about the thing of 1.3-micrometer resist thickness whose rate of a dimensional change of a resist pattern is 10% or less was made into x.

(6) In the light exposure to which the dense pattern of the variation-of-tolerance Rhine & tooth space 1:1 of roughness and fineness reproduces 0.35 micrometers, the difference of the dimension of the dense pattern of the Rhine & tooth space 1:1 and the non-dense pattern of 1:5 was evaluated. That to which it exceeded O and **0.5% for that whose non-dense pattern was less than **5% of dimensional change was made into x on the basis of the dimension of a dense pattern.

[0043] (Evaluation conditions) After applying the resist solution of the presentation shown in Table 1 by the spinner on a silicon wafer, prebaking was performed for 60 seconds at 90 degrees C, and 1.07 micrometers of thickness and the 1.3-micrometer resist film were formed in the wafer. After exposing carrying out adjustable [of the exposure time] for this wafer using i line stepper NSR2005i10D (NIKON CORP. make; NA=0.57) and REKUCHIRU for a test, BEKU after exposure (Post Exposure Baking) was performed for 60 seconds at 110 degrees C. Next, negatives were developed with 23 degrees C and the paddle method during 1 minute in 2.38% of tetramethylammonium hydroxide water solution, and the positive type pattern was formed. This wafer was taken out, it observed with the electron microscope, and

sensibility, a resolution pattern configuration, focal tolerance, and a dimensional change were observed. The presentation of each resist constituent and an evaluation result are shown in Table 2.

[0044]

[Table 1]

(表 1)

組成物	樹脂		感光剤1			感光剤2			ポリトキシ化合物		溶剤
	種類	添加量	種類	Mw	エステル添加量	種類	エステル添加量		種類	添加量	
1	A-2	87	B-1	5500	65 35	B-9	65 10		C-3	13	D-1
2	A-4	84	B-2	8000	50 20	B-9	65 45		C-1	16	D-1
3	A-6	85	B-3	6300	40 10	B-10	60 22		C-2	15	D-2
4	A-6	85	B-4	9700	35 20	B-10	60 30		C-2	15	D-2
5	A-2	87	B-5	8500	60 15	B-9	65 38		C-3	13	D-1
6	A-6	85	B-6	11100	55 15	B-11	80 32		C-1	15	D-2
7	A-6	85	B-5	8500	60 5	B-10	60 30		C-2	15	D-1
8	A-4	84	B-7	2300	75 39	—	—		C-2	16	D-2
9	A-6	85	B-8	13100	40 26	B-9	65 17		C-2	15	D-1

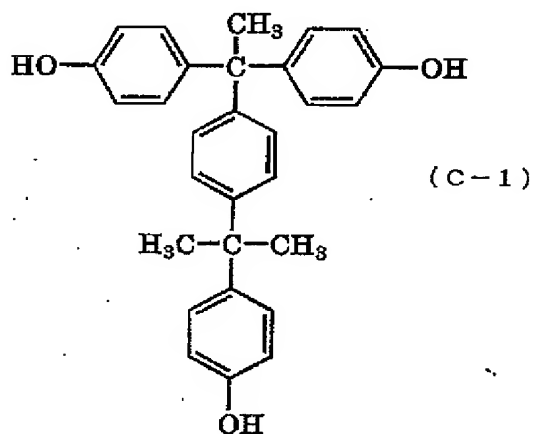
[0045] Explanation of the cable address of Table 1: The C-1= following type (C-1)

The C-2= following type (C-2)

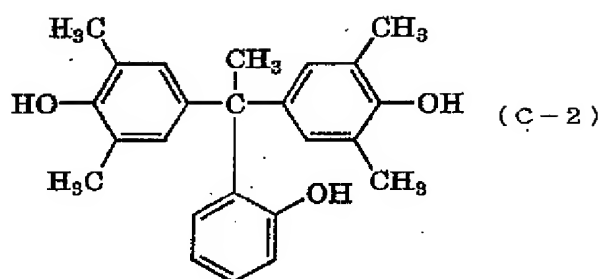
The C-3= following type (C-3)

D-1=2-hydroxy ethyl propionate D-2=3-methoxy methyl propionate [0046]

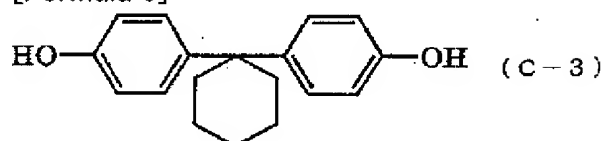
[Formula 7]



[Formula 8]



[Formula 9]



[0047]

[Table 2]

(表 2)

	組成物	A値	感度 (msec)	解像度 (μ m)	パターン 形状	フォーカス 許容性	寸法 変化	保存 安定性
実施例	1	0.35	220	0.28	○	○	○	○
	2	1.30	250	0.28	○	○	○	○
	3	0.70	212	0.28	○	○	○	○
	4	0.85	300	0.29	○	○	○	○
	5	1.11	298	0.28	○	○	○	○
	6	0.95	330	0.29	○	○	○	○
	7	0.85	240	0.28	○	○	△	○
比較例	8	1.00	220	0.29	△	×	×	○
	9	1.30	298	0.28	○	△	×	△

[0048] It excelled in sensibility, a resolution pattern configuration, and focal admissibility, and these results showed giving very few patterns of a dimensional change or variation of tolerance of condensation and rarefaction, even if the photoresist constituent of this invention was the case where a pattern was formed in the resist film with comparatively high thickness.

[0049]

[Effect of the Invention] Sensibility, resolution pattern configuration, and focal tolerance of the positive type photoresist constituent of this invention improve, it shows the resist property which was excellent even if it was thick-film conditions to suppress a dimensional change and variation of tolerance of condensation and rarefaction etc., and is excellent also in preservation stability. It is very useful to the integrated-circuit manufacture considered from this that, as for the constituent of this invention, high integration will progress further from now on.

[Translation done.]